A highly active bimetallic supported Rh–Co hydroformylation catalyst prepared from $RhCl_3$ and $Co_2(CO)_8$

L. Huang * and Y. Xu

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PO Box 110, 116023 Dalian, PR China

Received 29 July 1998; accepted 22 September 1998

The preparation of a highly active bimetallic SiO_2-supported Rh–Co catalyst from $RhCl_3$ and $Co_2(CO)_8$ ($Rh:Co = 1:3$ atomic ratio) has been studied by IR spectroscopy and ethylene hydroformylation, etc. Two steps are involved in the preparative process: (1) surface-mediated synthesis of $Rh^+(CO)_2/SiO_2$ from calcined $RhCl_3/SiO_2$; (2) impregnation of $Rh^+(CO)_2/SiO_2$ with a $Co_2(CO)_8$ solution followed by H_2 reduction at 623 K. The IR results of reductive carbonylation of calcined $RhCl_3/SiO_2$ have been compared to those of uncalcined $RhCl_3/SiO_2$ at 373 K. *In situ* IR observations, extraction results and elemental analysis suggest that approximately 50% of $RhCl_3$ are transformed to Rh_2O_3 on the SiO_2 surface and that calcined $RhCl_3/SiO_2$ is converted to a mixture of $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2O_s]_2$ (O_s: surface oxygen) under CO at 373 K. When this SiO_2-supported mixture was submitted to impregnation with a $Co_2(CO)_8$ solution at room temperature, IR study and elemental analysis show that $[Rh(CO)_2Cl]_2$ reacts easily with $Co_2(CO)_8$ on the surface to give $RhCo_3(CO)_{12}$, whereas $[Rh(CO)_2O_s]_2$ does not react with $Co_2(CO)_8$. Catalytic study in steady-state ethylene hydroformylation shows that a catalyst thus derived is more active than a catalyst derived from $RhCo_3(CO)_{12}/SiO_2$ and a catalyst derived by coimpregnation of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2. This result suggests that the high rhodium dispersion of $[Rh(CO)_2O_s]_2$ plays a crucial role in the formation of highly dispersed bimetallic Rh–Co sites.

Keywords: $RhCl_3$, $Co_2(CO)_8$, SiO_2, surface-bonded $Rh^+(CO)_2$, highly active Rh–Co catalyst, hydroformylation

1. Introduction

The preparation of highly active bimetallic catalysts has been attracting much attention in heterogeneous catalysis. It has been recognized that organometallic complexes possess advantages over inorganic salts as precursors in the preparation of inorganic material-supported bimetallic catalysts [1,2]. Using inorganic salts as precursors, it is difficult to obtain active bimetallic catalysts comparable to those derived from organometallic complexes or clusters for CO-based reactions such as Fischer–Tropsch synthesis and olefin hydroformylation [3–5]. In recent studies on the preparation of bimetallic Rh–Co hydroformylation catalysts, we found that the direct impregnation of $RhCl_3/SiO_2$ or Rh_2O_3/SiO_2 with a $Co_2(CO)_8$ solution cannot lead to the efficient formation of bimetallic $RhCo_3$ clusters and that a catalyst thus obtained is much less active than catalysts derived from $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ [5] and from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ [6]. By combination with $Co_2(CO)_8$, a non-carbonyl rhodium precursor shows so much difference from a carbonyl rhodium precursor in the production of a bimetallic Rh–Co catalyst. However, inorganic compounds like $RhCl_3$ and Rh_2O_3 are preferentially chosen as starting materials to prepare rhodium catalysts from economical point of view. We therefore attempted to convert first $RhCl_3$ (or Rh_2O_3) to $[Rh(CO)_2Cl]_2$ (or $[Rh(CO)_2O]_2$) on SiO_2 by surface-mediated carbonylation. Then the resulting $[Rh(CO)_2Cl]_2/SiO_2$ and $[Rh(CO)_2O]_2/SiO_2$ were subjected to impregnation with a $Co_2(CO)_8$ solution, thereby leading to highly active bimetallic Rh–Co catalysts. In this letter, we shall mainly describe the surface chemistry during the process of two-step preparation for a bimetallic SiO_2-supported Rh–Co catalyst from $RhCl_3$ and $Co_2(CO)_8$. We shall compare the related catalytic properties for ethylene hydroformylation to those obtained over bimetallic SiO_2-supported Rh–Co catalysts derived from $RhCo_3(CO)_{12}$ and from $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$.

2. Experimental

$RhCl_3{\cdot}nH_2O$ and $Co_2(CO)_8$ were purchased commercially. $[Rh(CO)_2Cl]_2$ and $RhCo_3(CO)_{12}$ were synthesized according to literature [7,8]. SiO_2 was a silica "Aerosil" supplied by Degussa with a surface area of 380 m^2/g. Dichloromethane and n-hexane used as solvents were distilled over P_2O_5 under Ar and stored over activated 5A molecular sieves under Ar. The gases H_2, CO, C_2H_4 and Ar had a purity of 99.99%. Before introduction into an IR cell, a sample vessel and a reactor, they were further purified by passage through traps of activated 5A molecular sieves and Mn/MnO.

Metal carbonyl catalyst precursors were prepared by impregnating SiO_2 with solutions of metal carbonyls. SiO_2 (60–80 mesh granule) was predehydroxylated under vacuum at 673 K for 5 h, and impregnated or coimpregnated with metal carbonyl(s) in dry n-hexane under Ar in a Schlenk tube. The impregnated systems were stirred for

---

* To whom correspondence should be addressed.

2 h under Ar. The solvent was removed by evacuation and the resulting solid samples were dried under vacuum (1.3×10^{-3} kPa) for 1 h. In this manner, $Co_4(CO)_{12}/SiO_2$, $[Rh(CO)_2Cl]_2/SiO_2$, $([Rh(CO)_2Cl]_2 + Co_4(CO)_{12})/SiO_2$ and $RhCo_3(CO)_{12}/SiO_2$ were made from $Co_2(CO)_8$, $[Rh(CO)_2Cl]_2$ and $RhCo_3(CO)_{12}$.

$RhCl_3/SiO_2$ and related catalyst precursors were prepared according to the following procedure. First, SiO_2 (60–80 mesh granule) was incipient wetted with a solution of $RhCl_3$. Then the resulting slurry after stirring was gently heated under an infrared lamp till it turned into a dry solid sample $RhCl_3/SiO_2$. For making a conventional rhodium catalyst, $RhCl_3/SiO_2$ was subjected to calcination in air at 673 K for 5 h. According to the colorimetric analysis, the percent of retained chlorine on the surface after calcination is 48%. Such oxidative calcination is believed to result in a partial conversion of $RhCl_3$ to Rh_2O_3 [9]. For making a binary catalyst from $RhCl_3$ and $Co_2(CO)_8$, calcined $RhCl_3/SiO_2$ was outgassed under vacuum (1.3×10^{-3} kPa) at room temperature for 2 h and subsequently impregnated with a n-hexane solution of $Co_2(CO)_8$ under Ar in a Schlenk tube. The impregnated system was stirred for 2 h under Ar followed by removal of the solvent under vacuum. The resulting solid sample was dried under vacuum (1.3×10^{-3} kPa) for 1 h. For the surface-mediated synthesis of rhodium gem-dicarbonyl $Rh^+(CO)_2$, both uncalcined $RhCl_3/SiO_2$ and calcined $RhCl_3/SiO_2$ were used to react with 91 kPa of static CO at 373 K in Schlenk vessels. In the case of uncalcined $RhCl_3/SiO_2$, $RhCl_3/SiO_2$ (1.0 g) was outgassed under vacuum (1.3×10^{-3} kPa) at room temperature for 2 h and subsequently exposed to CO. After the system had been heated at 373 K for 1 h, the solid sample turned yellow. In the case of calcined $RhCl_3/SiO_2$, calcined $RhCl_3/SiO_2$ (1.0 g) was rehydrated by standing in air at room temperature for 10 h, since the water content had been found to play an important role in the reductive conversion of Rh^{3+} to $Rh^+(CO)_2$ under CO [10–13]. Subsequently, it was outgassed under vacuum (1.3×10^{-3} kPa) at room temperature for 2 h before exposure to CO. After the system had been heated at 373 K for 24 h, the solid sample turned light yellow. In order to make a binary catalyst from $Rh^+(CO)_2/SiO_2$ thus produced and $Co_2(CO)_8$, $Rh^+(CO)_2/SiO_2$ carbonylated from calcined $RhCl_3/SiO_2$ was chosen to be impregnated with a n-hexane solution of $Co_2(CO)_8$ under Ar in a Schlenk tube. The impregnated system was stirred for 2 h under Ar followed by removal of the solvent under vacuum. The resulting solid sample was dried under vacuum (1.3×10^{-3} kPa) for 1 h.

All rhodium catalyst precursors prepared contained 1% Rh. The loading of cobalt in related catalyst precursors was 1.7. The atomic ratio of Rh : Co was 1 : 3 in binary catalyst precursors.

Hydroformylation of ethylene was conducted under atmospheric pressure at 423 K in a glass tubing-flow reactor (i.d. = 7 mm) where 0.10 g of catalyst precursor was charged. The catalyst precursors containing metal carbonyls were transferred to the reactor under Ar. The catalyst precursors were treated in flowing H_2 at 623 K for 2 h and, subsequently, H_2 was replaced by a mixture of C_2H_4, CO and H_2 (20 : 20 : 20 ml/min) at 423–473 K. The conversion of C_2H_4 was controlled to below 15%. Both hydrocarbon and oxygenated products were analyzed on line with gas chromatography, using a 2 m length column of Porapak R and a flame ionization detector.

IR experiments were carried out using a KBr cell for liquid samples and a single beam cell with CaF_2 windows for solid samples. For the monitoring of surface-mediated synthesis of $Rh^+(CO)_2/SiO_2$ from Rh^{3+}/SiO_2, the above mentioned uncalcined $RhCl_3/SiO_2$ and calcined $RhCl_3/SiO_2$ were pressed into wafers of 20 mg each and placed in the IR cell. Following 2 h of outgassing under vacuum (1.3×10^{-3} kPa) at room temperature, the wafers were exposed to 13 kPa of CO and, subsequently, the temperature was raised to 373 K as rapidly as possible. All IR spectra were recorded on a Bio-Rad FTS-7 spectrometer at room temperature. Surface IR spectra were measured in the presence of gas phases by subtracting the contributions of solid and gas phases.

The metal contents of the samples studied were determined by X-ray fluorescence and atomic absorption spectroscopies. Analysis of chlorine contents was performed by colorimetric method. According to analytical results, the metal contents of all the catalysts studied remained unchanged before and after catalytic tests.

3. Results

3.1. IR studies on the formation of bimetallic SiO_2-supported Rh–Co catalysts from $RhCl_3$ and $Co_2(CO)_8$

First of all, we checked the surface reaction of Rh^{3+}/SiO_2 with CO *in situ* by IR spectroscopy. Figure 1 shows the *in situ* surface IR spectra obtained during the carbonylation of uncalcined $RhCl_3/SiO_2$ under 13 kPa of CO at 373 K. Upon initiation of the reaction at 373 K, the wafer displayed three weak bands at 2147, 2111 and 2043 cm^{-1} in the ν(CO) region. The 2147 cm^{-1} band is assigned to the linear CO adsorbed on Rh^{3+}/SiO_2. Although the 2111 cm^{-1} band was apparently more intense than the 2043 cm^{-1} band throughout the carbonylation, they increased synchronously in intensity with reaction time. Therefore, these two bands are attributed to the symmetrical and asymmetrical C–O stretching of rhodium gem-dicarbonyl adsorbed on SiO_2 [14]. The 2111 and 2043 cm^{-1} bands grew quite rapidly as the reaction proceeded whereas the 2147 cm^{-1} band disappeared gradually. The conversion of Rh^{3+} to $Rh^+(CO)_2$ on the SiO_2 surface reached a chemical equilibrium within 40 min, judging from the constant band intensity observed in figure 1 (d) and (e).

Figure 2 shows the *in situ* surface IR spectra taken during the carbonylation of calcined $RhCl_3/SiO_2$ (rehydrated)

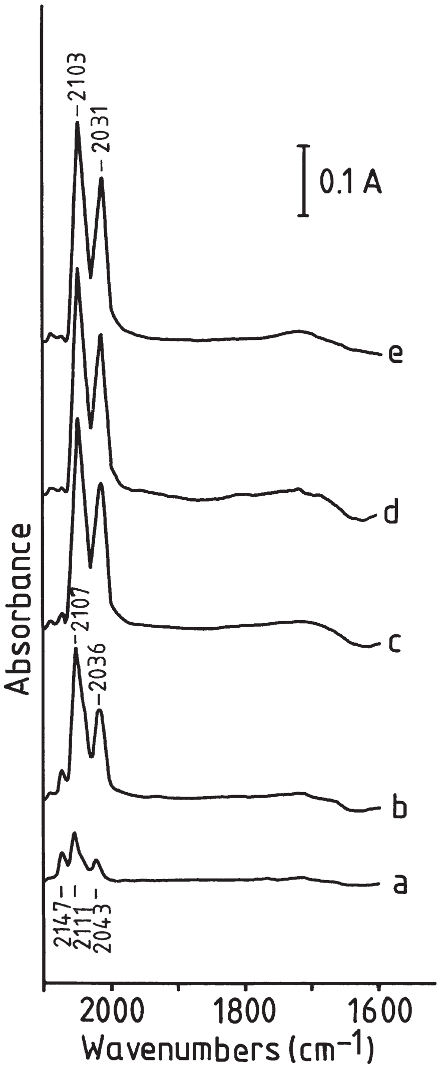


Figure 1. Surface IR spectra during the carbonylation of uncalcined $RhCl_3/SiO_2$ under 13 kPa of CO at 373 K. (a) 3 min, (b) 10 min, (c) 20 min, (d) 40 min, (e) 1 h.

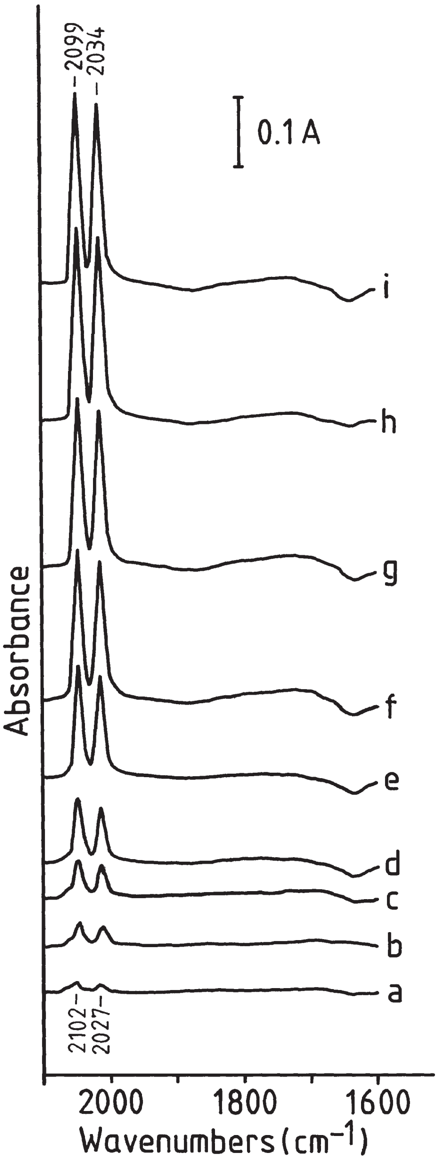


Figure 2. Surface IR spectra during the carbonylation of calcined $RhCl_3/SiO_2$ under 13 kPa of CO at 373 K. (a) 3 min, (b) 10 min, (c) 20 min, (d) 1 h, (e) 3 h, (f) 6 h, (g) 10 h, (h) 22 h, (i) 27 h.

under 13 kPa of CO at 373 K. As soon as the reaction was initiated at 373 K, the surface spectrum exhibited two rather weak bands at 2102 and 2027 cm^{-1} in the ν(CO) region, which increased synchronously in intensity with reaction time. They correspond to $Rh^+(CO)_2/SiO_2$. In contrast with the case of uncalcined $RhCl_3/SiO_2$, the gem-dicarbonyl bands developed slowly under CO with reaction time. According to the observed spectral intensity, the transformation of Rh^{3+} to $Rh^+(CO)_2$ did not attain to a maximum until 22 h of reaction. Throughout the carbonylation, it was noted that the two bands had almost equal integrated intensity.

In order to reveal the natures of calcined $RhCl_3/SiO_2$ and $Rh^+(CO)_2$ on the surface made from calcined $RhCl_3/SiO_2$, we conducted extraction experiments toward $Rh^+(CO)_2/SiO_2$ made from both uncalcined $RhCl_3/SiO_2$ and calcined $RhCl_3/SiO_2$. In the case of uncalcined $RhCl_3/SiO_2$, $RhCl_3/SiO_2$ (1.0 g) was outgassed under vacuum (1.3×10^{-3} kPa) at room temperature for 2 h before exposure to 91 kPa of CO. Then the system was heated at 373 K for 1 h. The solid sample was observed to turn yellow and was transferred to a Schlenk tube under Ar. An organic solvent was added to the Schlenk tube under Ar for extraction. In the case of calcined $RhCl_3/SiO_2$, calcined $RhCl_3/SiO_2$ (1.0 g) was rehydrated by standing in air at room temperature for 10 h and subsequently outgassed under vacuum (1.3×10^{-3} kPa) at room temperature for 2 h before exposure to 91 kPa of CO. After the system had been heated at 373 K for 24 h, the solid sample turned light yellow and was transferred to a Schlenk tube under Ar. An organic solvent was added to the Schlenk tube for extraction. From both sample surfaces, yellow adspecies could be extracted into either n-hexane or dichloromethane. The yellow extracts exhibited the same IR bands at 2119w, 2097s and 2039s in dichloromethane, which are characteristic of $[Rh(CO)_2Cl]_2$. The solid samples were washed with dichloromethane for three times. Based on the chlorine analysis of the solid samples, the yield of $[Rh(CO)_2Cl]_2$ from uncalcined $RhCl_3/SiO_2$ was 85%, whereas that from calcined $RhCl_3/SiO_2$ was only 39% (only 8% of chlorine were retained in the calcined sample). The results seem to indicate that more than half of Rh^{3+} ions interact strongly with surface OH^- groups of SiO_2 with the concomitant loss of Cl^- ions when $RhCl_3/SiO_2$ is calcined in air at a temperature of 673 K.

The yield of 85% for $[Rh(CO)_2Cl]_2$ obtained from uncalcined $RhCl_3/SiO_2$ indicated that $RhCl_3$ can be nearly completely converted to $[Rh(CO)_2Cl]_2$ on SiO_2 by surface-mediated carbonylation since there is more or less part of $[Rh(CO)_2Cl]_2$ remaining adsorbed on the surface after extraction with dichloromethane. Accordingly, the surface-mediated synthesis of $[Rh(CO)_2Cl]_2/SiO_2$ from uncalcined $RhCl_3/SiO_2$ is essentially equivalent to $[Rh(CO)_2Cl]_2/SiO_2$ made by impregnation of $[Rh(CO)_2Cl]_2$ on SiO_2. Combining the *in situ* IR data and extraction results, we suggest that an important part of $Rh^+(CO)_2$ produced from calcined $RhCl_3/SiO_2$ is anchored to the surface of SiO_2. We shall focus our study on the SiO_2-anchored $Rh^+(CO)_2$ and compare its behavior to that of $[Rh(CO)_2Cl]_2/SiO_2$ made from $[Rh(CO)_2Cl]_2$ in the formation of bimetallic Rh–Co catalysts in the following.

1.0 g of $Rh^+(CO)_2/SiO_2$ (1% Rh loading) was first prepared by carbonylation of calcined $RhCl_3/SiO_2$ in a Schlenk vessel as depicted above. Then a solution of $Co_2(CO)_8$ (61.2 mg) in n-hexane (5 ml) was introduced into the Schlenk vessel under Ar. The liquid–solid system was stirred for 10 min and stood for 2 h. The solvent was removed by evacuation followed by 2 h of treatment under vacuum (1.3×10^{-3} kPa). The resultant solid sample (1% Rh loading, $Rh:Co = 1:3$ atomic ratio) was transferred into a clean Schlenk tube under Ar. n-hexane was added inside the Schlenk tube under Ar. Figure 3(a) represents the carbonyl spectrum of the obtained brown extract. The spectrum contains bands at 2065s, 2059s, 2039w, 2030w, 1913vw, 1887w and 1863m cm^{-1}.

After a careful comparison of the spectra for $RhCo_3(CO)_{12}$ and $Co_4(CO)_{12}$ (figure 3 (b) and (c)), we reckon that the spectrum in figure 3(a) is likely to comprise the bands of $Co_4(CO)_{12}$ and the bands of $RhCo_3(CO)_{12}$. Although quite similar linear carbonyl bands make identification difficult, the markedly different band intensities observed at 1887 and 1863 cm^{-1} suggest the weak 1887 cm^{-1} band belongs to one of the main bridged carbonyl features for $RhCo_3(CO)_{12}$ and the intense 1863 cm^{-1} band consists of another main bridged carbonyl feature for $RhCo_3(CO)_{12}$ and the main bridged carbonyl feature for $Co_4(CO)_{12}$. It is interesting to note that neither the bands of $[Rh(CO)_2Cl]_2$ nor the bands of $Co_2(CO)_8$ were present in this spectrum. According to the elemental analysis for rhodium, the percent of rhodium species extracted from the SiO_2 surface was 40–50.

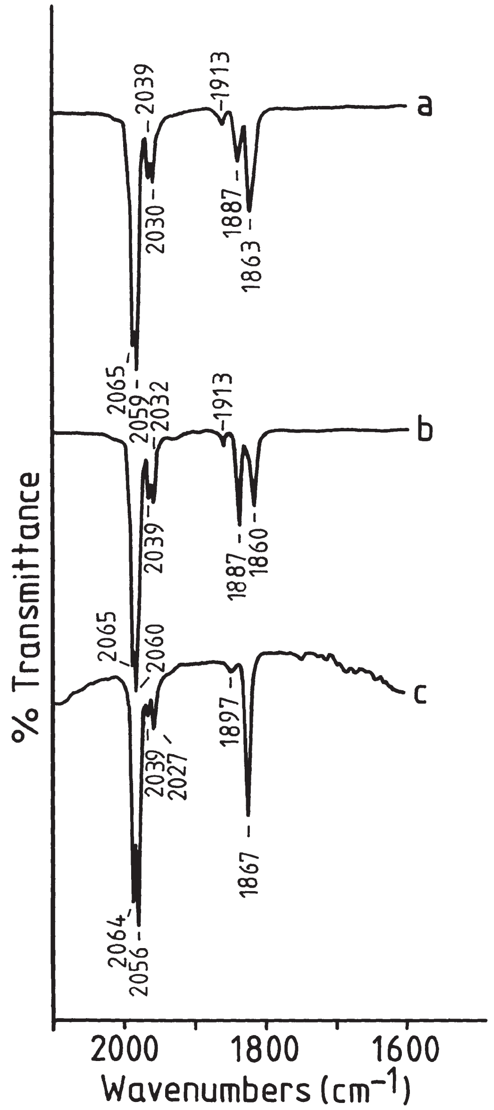


Figure 3. IR spectra of metal carbonyls in n-hexane. (a) Extract from the surface (1% Rh loading) after impregnation of $Rh^+(CO)_2/SiO_2$ derived from calcined $RhCl_3/SiO_2$ with a n-hexane solution of $Co_2(CO)_8$ ($Rh:Co = 1:3$ atomic ratio) followed by 2 h of treatment under vacuum (1.3×10^{-3} kPa) at 293 K; (b) $RhCo_3(CO)_{12}$; (c) $Co_4(CO)_{12}$.

3.2. Catalytic test in ethylene hydroformylation

The understanding of the formation of bimetallic Rh–Co clusters or particles should gain support from the catalytic study. Table 1 gives comparative results of ethylene hydroformylation over a variety of SiO_2-supported catalysts under atmospheric pressure at 423 K. Under the same catalytic conditions, addition of cobalt to Rh/SiO_2 led to significant increase in hydroformylation activity to different extent. Moreover, the selectivity to oxygenates was markedly improved.

It is noteworthy that the catalyst derived by addition of $Co_2(CO)_8$ to $Rh^+(CO)_2/SiO_2$ carbonylated from calcined $RhCl_3/SiO_2$ was nineteen times more active than Rh/SiO_2 for the formation of oxygenates. This activity actually surpasses that of the catalyst derived by impregnation of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2. We also determined

Table 1

Catalytic properties of SiO_2-supported catalysts[a] in atmospheric ethylene hydroformylation ($C_2H_4 : CO : H_2 = 20 : 20 : 20$ ml/min) at 423 K.

Starting material	Co : Rh (atomic ratio)	Activity[b]		Selectivity (mol%)		
		C_2H_6	Oxygenates[c]	C_2H_5CHO	n-C_3H_7OH	C_2H_6
$Co_2(CO)_8$		0	0	–	–	–
$RhCl_3$		0.39	0.28	41	0	59
$[Rh(CO)_2Cl]_2$		0.43	0.27	39	0	61
$RhCl_3 + Co_2(CO)_8$	3 : 1	0.88	1.40	53	8	39
$(RhCl_3 + Co_2(CO)_8)$[d]	3 : 1	3.00	5.44	56	8	36
$[Rh(CO)_2Cl]_2 + Co_2(CO)_8$	3 : 1	3.85	5.00	51	5	44
$RhCo_3(CO)_{12}$		3.63	6.56	58	6	36

[a] With 1% Rh and 1.7% Co loadings, pretreated under H_2 at 623 K for 2 h.

[b] Expressed by (mol/Co mol/min) for Co/SiO_2- and (mol/Rh mol/min) for Rh-containing catalysts, data were taken 7 h after the initiation of reaction.

[c] $C_2H_5CHO + n$-C_3H_7OH.

[d] $RhCl_3/SiO_2$ was precalcined in air at 673 K for 5 h and carbonylated under 91 kPa of CO at 373 K for 24 h before impregnation with a $Co_2(CO)_8$ solution.

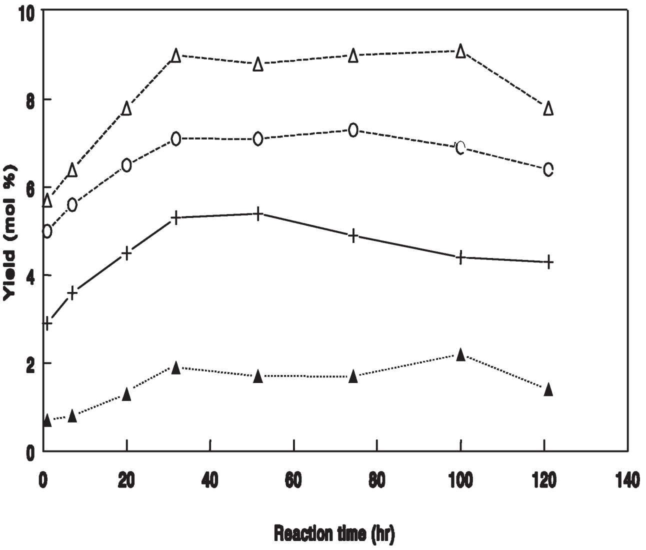


Figure 4. Dynamic atmospheric ethylene hydroformylation ($C_2H_4 : CO : H_2 = 20 : 20 : 20$ ml/min) at 423 K over a catalyst derived from $Rh^+(CO)_2/SiO_2$ and $Co_2(CO)_8$ (1% Rh loading, Rh : Co = 1 : 3 atomic ratio). (+) C_2H_6, (○) C_2H_5CHO, (▲) n-C_3H_7OH, (△) $C_2H_5CHO + n$-C_3H_7OH.

the catalytic yields of different products as a function of reaction time over this catalyst, as shown in figure 4. It is clearly seen that this catalyst did display high catalytic activity and good catalytic stability during 121 h of reaction. As compared with the case of the $RhCo_3(CO)_{12}$-derived catalyst [15], although the activity to oxygenates over this catalyst was slightly lower than that over the $RhCo_3(CO)_{12}$-derived catalyst before 20 h of reaction, afterward it increased and evidently surpassed that over the $RhCo_3(CO)_{12}$-derived catalyst till the reaction ceased. Furthermore, it seems that this catalyst is actively more stable than the $RhCo_3(CO)_{12}$-derived catalyst throughout the reaction. Also it was noticed that the yields of oxygenates over this catalyst are slightly higher than those over the catalyst derived by impregnation of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2 during ethylene hydroformylation on stream [6].

Comparatively, in the case with the direct addition of $Co_2(CO)_8$ to $RhCl_3/SiO_2$, the activity to oxygenates was only increased by four times compared to that of Rh/SiO_2. This result is much less satisfactory than in the case with the addition of $Co_2(CO)_8$ to $Rh^+(CO)_2/SiO_2$.

Therefore, the catalyst derived by addition of $Co_2(CO)_8$ to $Rh^+(CO)_2/SiO_2$ carbonylated from calcined $RhCl_3/SiO_2$ exhibits unusual hydroformylation activity and stability.

4. Discussion

The gas–solid-phase reaction of $RhCl_3 \cdot nH_2O$ with CO at moderate temperature is a spontaneous and efficient process for producing $[Rh(CO)_2Cl]_2$. McCleverty and Wilkinson earlier described that this reaction proceeds at 373 K and atmospheric pressure according to the following equation:

$$2(RhCl_3 \cdot 3H_2O) + 6CO \xrightarrow{373\ K} [Rh(CO)_2Cl]_2 + 6H_2O + 2COCl_2 \tag{1}$$

and the reaction is complete with a $[Rh(CO)_2Cl]_2$ yield of 96% after 3–5 h [7]. Using the surfaces of inorganic oxides such as SiO_2, Al_2O_3 and zeolites as reaction media, the formation of $Rh^+(CO)_2$ from $RhCl_3$ under CO is obviously promoted and the reaction can take place at room temperature and pressures below 1 atm [10–12,16–19]. Since both water and OH^- of the surfaces were found to be involved in the formation of $Rh^+(CO)_2$ from adsorption of CO on supported $RhCl_3$, two reactions were suggested on the surfaces as follows [10–12]:

$$Rh^{3+} + 3CO + H_2O \rightarrow Rh^+(CO)_2 + 2H^+ + CO_2 \tag{2}$$

$$Rh^{3+} + 3CO + OH^- \rightarrow Rh^+(CO)_2 + H^+ + CO_2 \tag{3}$$

Roberto et al. carbonylated SiO_2-supported $RhCl_3 \cdot nH_2O$ (1.5–5% Rh loadings) at room temperature and atmospheric pressure and extracted $[Rh(CO)_2Cl]_2$ formed from the surface with dichloromethane or acetone [13]. They obtained higher yields of 80–84% in the presence of water after

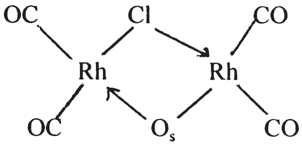
24 h of reaction [13]. The experimental conditions are apparently milder than those under which McCleverty and Wilkinson prepared $[Rh(CO)_2Cl]_2$ directly from carbonylation of unsupported $RhCl_3{\cdot}nH_2O$ [7].

Great attention has been paid to the study of $Rh^+(CO)_2$ and $[Rh(CO)_2Cl]_2$ on inorganic supports because of application in industrial catalytic reactions, especially olefin hydroformylation [10–12,14,16–30]. Among numerous publications of the past decade, much work is devoted to the surface-mediated synthesis of $[Rh(CO)_2Cl]_2$ from supported $RhCl_3{\cdot}nH_2O$ [10,12,13,17–20] and to the reactivity of $Rh^+(CO)_2$ species [12,28–30]. Little work has been done on the interaction of rhodium chlorides with support surfaces and the association of different interactions with catalytic properties. In general, the catalytic activity and selectivity of final supported catalysts are influenced by the form of $Rh^+(CO)_2$ or Rh^{3+} on a surface. $Rh^+(CO)_2$ can be present as $[Rh(CO)_2Cl]_2$ and $[Rh(CO_2O_s]_2$ on the SiO_2 surface [17,18]. Maximum metal dispersion would be expected for $[Rh(CO)_2O_s]_2$ because the bridging ligands between the metal centers are inherent to the surface, while the chlorine-bridged $[Rh(CO)_2Cl]_2$ might more readily form three-dimensional aggregates [18].

In the present study, the two different pretreatments for $RhCl_3/SiO_2$ result in distinct IR behaviors in carbonylation, distinct reactivities of $Rh^+(CO)_2/SiO_2$ with $Co_2(CO)_8$ and distinct catalytic properties for ethylene hydroformylation over the catalysts derived from $Rh^+(CO)_2/SiO_2$ and $Co_2(CO)_8$. In the case of uncalcined $RhCl_3/SiO_2$, chlorine is entirely retained on the surface. Reductive carbonylation of $RhCl_3$ on SiO_2 at 373 K produces efficiently and rapidly $[Rh(CO)_2Cl]_2/SiO_2$. The surface reaction is complete within only 40 min and much faster than the reaction occurring at the same temperature from unsupported $RhCl_3{\cdot}nH_2O$ [7]. This accounts for the positive influence of the SiO_2 surface on the rate of formation of $[Rh(CO)_2Cl]_2$. The surface-mediated synthesized $[Rh(CO)_2Cl]_2$ not only exhibits its characteristic features at 2103 and 2031 cm^{-1} on SiO_2, but also is extracted from the surface into dichloromethane in a yield as high as 85%. This is entirely in agreement with a number of previous studies by others [12,13,16–19]. The fact that a small amount of chlorine (15%) is detected on the SiO_2 surface after extraction of $[Rh(CO)_2Cl]_2$ suggests that almost all the $RhCl_3$ is transformed to $[Rh(CO)_2Cl]_2$ on SiO_2 under the action of CO and only a small part of $[Rh(CO)_2Cl]_2$ adsorbed on SiO_2 is not extracted into the solvent. $[Rh(CO)_2Cl]_2/SiO_2$ so obtained has little difference from that made by impregnation of $[Rh(CO)_2Cl]_2$ on SiO_2. In the case of calcined $RhCl_3/SiO_2$, however, there is an important loss of chlorine from $RhCl_3$, probably due to the reaction with O_2 in air to release Cl_2 [31] and the interaction with surface OH^- to liberate HCl [32]. Precise reactivities of $RhCl_3$ supported on SiO_2 with O_2 and surface OH^- under calcination conditions have not yet been elucidated. Earlier work indicated that $RhCl_3{\cdot}nH_2O$ is decomposed to sesquioxide and HCl from above 373 K in air [32]; Gloor and Prins, who recently determined the chemisorption of chlorine on Rh/SiO_2 prepared from $[Rh(NH_3)_5Cl]Cl_2$ by EXAFS study, suggested that each rhodium ion retains one chlorine ion and obtains five oxygen anions in its first coordination shell after calcination at 673 K [9]. However, Chuang and Debnath, who prepared $RhCl_3/SiO_2$ by treating $RhCl_3{\cdot}0.7H_2O/SiO_2$ under N_2 at 473 K, did not reckon that $RhCl_3$ is decomposed on the SiO_2 surface under operating conditions [12]. In our case, the surface of $RhCl_3/SiO_2$ prepared by incipient wetness technique contains an abundance of water. After 5 h of calcination in air at 673 K, 53% of chlorine evolve based on the elemental analysis. According to the extraction result of $[Rh(CO)_2Cl]_2$, the remaining chlorine is believed to be present as $[Rh(CO)_2Cl]_2$ following reductive carbonylation of calcined $RhCl_3/SiO_2$ at 373 K. These results show that $RhCl_3$ is far from being completely transformed to Rh_2O_3 and nearly half of $RhCl_3$ are still retained on the SiO_2 surface under operating calcination conditions. The existence of $RhCl_3$ on calcined $RhCl_3/SiO_2$ and the formation of $[Rh(CO)_2Cl]_2$ from such a surface may be supported by the fact that $RhCo_3(CO)_{12}$ can be extracted from the surface by n-hexane following 2 h of contact between $Rh^+(CO)_2/SiO_2$ and $Co_2(CO)_8$, as shown in figure 3. The production of $RhCo_3(CO)_{12}$ is indicative of the consumption of $[Rh(CO)_2Cl]_2$ by the action with $Co_2(CO)_8$ on the surface according to the following equation:

$$2[Rh(CO)_2Cl]_2 + 7Co_2(CO)_8 \rightarrow 4RhCo_3(CO)_{12} + 2CoCl_2 + 16CO \qquad (4)$$

which was proposed by our very recent study [6]. This reaction proceeds quite rapidly on the SiO_2 surface and can be complete within a few minutes [6]. At the same time, the observation of $Co_4(CO)_{12}$ and the absence of $[Rh(CO)_2Cl]_2$ in the extract solution indicate that added $Co_2(CO)_8$ is actually stoichiometrically excessive with respect to $[Rh(CO)_2Cl]_2$ so that it is naturally converted to $Co_4(CO)_{12}$ [33] as well as $RhCo_3(CO)_{12}$ on SiO_2. Note that the amount of $Co_2(CO)_8$ used is stoichiometrically equivalent to that of $RhCl_3$ used in the formation of $RhCo_3(CO)_{12}$. This IR result is in marked contrast with the extraction result for the reaction between $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2 at an atomic ratio of $Rh:Co = 1:3.5$ [6]. In the latter case, the extract solution displays an IR spectrum well characteristic of $RhCo_3(CO)_{12}$ [6].



Apart from $[Rh(CO)_2Cl]_2$, it is possible that surface-anchored rhodium gem-dicarbonyl species such as $[Rh(CO)_2O_s]_2$ and arise from carbonylation of calcined $RhCl_3/SiO_2$. Although these rhodium gem-dicarbonyl species display the same doublet IR features as those of $[Rh(CO)_2O_s]_2/SiO_2$ [12,18], they are bonded to the surface of SiO_2 and cannot be extracted by an organic solvent [18]. As a result of the interactions of $RhCl_3$ with O_2 and surface OH^- during calcination in air at 673 K, part of this chlorine are replaced by surface oxygen thus resulting in a mixture of $RhCl_3$ and Rh_2O_3. When this mixture is subjected to carbonylation, the observed rate of formation of rhodium gem-dicarbonyl species is much lower than that of pure $[Rh(CO)_2Cl]_2$ on SiO_2, as shown by the comparative IR results in figures 1 and 2. This shows that the reductive carbonylation of Rh^{3+} in calcined $RhCl_3/SiO_2$ requires to be more strongly activated. The slower transformation of Rh^{3+} to $Rh^+(CO)_2$ on calcined $RhCl_3/SiO_2$ under CO is most likely related to the influence of surface oxygen, namely to the interaction between Rh^{3+} and surface oxygen. Inspection of the comparable IR spectral intensities in figures 1 and 2 after completion of carbonylation shows that almost all the Rh^{3+} ions in calcined $RhCl_3/SiO_2$ are transformed to $Rh^+(CO)_2$ species. Taking into consideration trace amounts of chlorine retained on the surface after extraction of $[Rh(CO)_2Cl]_2$ from the calcined sample, we infer that $Rh^+(CO)_2$ species thus produced are probably in the forms of $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2O_s]_2$. The latter possesses high rhodium dispersion on SiO_2 as it is bonded to the surface oxygen. According to the extraction result following the surface reaction between $Rh^+(CO)_2/SiO_2$ and $Co_2(CO)_8$, $[Rh(CO)_2O_s]_2$ does not seem to be reactive with $Co_2(CO)_8$ to give $RhCo_3(CO)_{12}$ at room temperature. However, the catalytic results in steady-state ethylene hydroformylation indicate that the catalyst derived by addition of $Co_2(CO)_8$ to $Rh^+(CO)_2/SiO_2$ is practically more active than the catalyst derived from $RhCo_3(CO)_{12}/SiO_2$ and the catalyst derived by coimpregnation of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2. The results suggest that such a higher catalytic activity results not only from the efficient formation of bimetallic Rh–Co clusters or particles, but also from the high dispersion of bimetallic Rh–Co clusters or particles on the SiO_2 surface. In recent studies regarding the preparation of SiO_2-supported bimetallic Rh–Co catalysts, we demonstrated that bimetallic Rh–Co clusters or particles can be efficiently produced from rhodium carbonyls and cobalt carbonyls [5,6,34,35] and can be formed only to a small extent from rhodium and cobalt inorganic salts [5]. We also showed that the enhancement of hydroformylation activity over a binary rhodium and cobalt catalyst compared to that over a monometallic rhodium catalyst is attributed to the bimetallic catalysis of Rh–Co clusters or particles [5]. In the case of calcined $RhCl_3/SiO_2$, the reaction of supported $Rh^+(CO)_2$ with $Co_2(CO)_8$ at room temperature yields only a part of bimetallic clusters in the form of $RhCo_3(CO)_{12}$, as shown significantly by the IR result. Another part of bimetallic Rh–Co clusters or particles are probably formed from the interaction of $[Rh(CO)_2O_s]_2$ with $Co_4(CO)_{12}$ at elevated temperatures under H_2. Such bimetallic Rh–Co sites are more dispersed so that the obtained catalyst is more active on the whole. From this work, we speculate that if the proportion of surface oxygen-bonded $Rh^+(CO)_2$ is increased on SiO_2, the resultant bimetallic Rh–Co catalyst has higher dispersion and thus higher catalytic activity.

5. Conclusions

A highly active bimetallic SiO_2-supported Rh–Co catalyst has been successfully prepared from $RhCl_3$ and $Co_2(CO)_8$ ($Rh:Co = 1:3$ atomic ratio) by two steps: (1) reductive carbonylation of calcined $RhCl_3/SiO_2$ to form $Rh^+(CO)_2/SiO_2$; (2) impregnation of $Rh^+(CO)_2/SiO_2$ with a $Co_2(CO)_8$ solution followed by H_2 reduction at 623 K. After 5 h of calcination in air at 673 K, nearly 50% of $RhCl_3$ are converted to Rh_2O_3 on SiO_2. Calcined $RhCl_3/SiO_2$ is converted to a mixture of $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2O_s]_2$ by the action of CO at 373 K. Upon impregnation of this SiO_2-supported mixture with a n-hexane solution of $Co_2(CO)_8$ at room temperature, adsorbed $[Rh(CO)_2Cl]_2$ reacts readily with $Co_2(CO)_8$ to produce $RhCo_3(CO)_{12}$, while $[Rh(CO)_2O_s]_2$ does not react with $Co_2(CO)_8$. The catalyst derived from $Rh^+(CO)_2/SiO_2$ and $Co_2(CO)_8$ is more active than the catalyst derived from $RhCo_3(CO)_{12}/SiO_2$ and the catalyst derived by coimpregnation of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2 in steady-state ethylene hydroformylation. The high catalytic activity may be ascribed to the high rhodium dispersion of $[Rh(CO)_2O_s]_2$ which leads to the formation of highly dispersed bimetallic Rh–Co sites through the interaction with cobalt atoms under H_2 at elevated temperatures.

Acknowledgement

The authors acknowledge the support of this research by the Chinese Academy of Sciences.

References

[1] J.M. Basset, B.C. Gates, J.P. Candy, A. Choplin, M. Leconte, F. Quignard and C.C. Santini, *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis* (Kluwer, Dordrecht, 1988).

[2] M. Ichikawa, Adv. Catal. 38 (1992) 283.

[3] M. Ichikawa, Polyhedron 127 (1988) 235.

[4] A. Fukuoka, L.F. Rao, N. Kosugi, H. Kurada and M. Ichikawa, Appl. Catal. 50 (1989) 295.

[5] L. Huang, J. Mol. Catal. A 125 (1997) 47.

[6] L. Huang and Y. Xu, Catal. Lett. 53 (1998) 177.

[7] J.A. McCleverty and G. Wilkinson, Inorg. Synth. 8 (1965) 211.

[8] S. Martinengo, G. Giordano and P. Chini, J. Organomet. Chem. 59 (1973) 379.

[9] A.P. Gloor and R. Prins, J. Phys. Chem. 98 (1994) 9865.

[10] J.C. Conesa, M.T. Sainz, J. Soria, G. Munuera, V. Rives-Arnau and A. Munoz, J. Mol. Catal. 17 (1982) 231.

[11] N. Takahashi, A. Mijin, H. Suematsu, S. Shinohara and H. Matsuoka, J. Catal. 117 (1989) 348.

[12] S.S.C. Chuang and S. Debnath, J. Mol. Catal. 79 (1993) 323.

[13] D. Roberto, R. Psaro and R. Ugo, Organometallics 12 (1993) 2292.

[14] C.A. Rice, S.D. Worley, C.W. Curtis, J.A. Guin and A.R. Tarrer, J. Chem. Phys. 74 (1981) 6487.

[15] L. Huang, A. Liu and Y. Xu, J. Mol. Catal. A 124 (1997) 57.

[16] M.S. Scurrell, J. Mol. Catal. 10 (1981) 57.

[17] M.P. Keyes and K.L. Watters, J. Catal. 100 (1986) 477.

[18] M.P. Keyes and K.L. Watters, J. Catal. 110 (1988) 96.

[19] R. Psaro, D. Roberto, R. Ugo, C. Dossi and A. Fusi, J. Mol. Catal. 74 (1992) 391.

[20] A. Krzywicky and M. Marczewsky, J. Mol. Catal. 6 (1979) 431.

[21] A.C. Yang and C.W. Garland, J. Phys. Chem. 61 (1957) 1504.

[22] J.T. Yates, Jr., T.M. Duncan, S.D. Worley and R.W. Vaughn, J. Chem. Phys. 70 (1979) 1219.

[23] P.R. Antoniewicz, R.R. Cavanagh and J.T. Yates, Jr., J. Chem. Phys. 73 (1980) 3456.

[24] S.D. Worley, C.A. Rice, G.A. Mattson, C.W. Curtis, J.A. Guin and A.R. Tarrer, J. Chem. Phys. 76 (1982) 20.

[25] P. Basu, D. Panayotov and J.T. Yates, Jr., J. Chem. Phys. 91 (1987) 3133.

[26] F. Solymosi and M. Pasztor, J. Phys. Chem. 89 (1985) 4789.

[27] A.K. Smith, F. Hugues, A. Theolier, J.M. Basset, R. Ugo, G.M. Zanderighi, J.L. Bilhou, V. Bilhou-Bougnol and W.F. Graydon, Inorg. Chem. 18 (1979) 3104.

[28] S.S.C. Chuang, G. Srinivas and A. Mukherjee, J. Catal. 139 (1993) 490.

[29] S.S.C. Chuang and S.I. Pien, J. Catal. 135 (1992) 618.

[30] G. Srinivas and S.S.C. Chuang, J. Phys. Chem. 98 (1994) 3024.

[31] S.E. Livingstone, in: *Comprehensive Inorganic Chemistry*, Vol. 3, eds. J.C. Bailar, Jr. et al. (Pergamon Press, Oxford, 1973) p. 1163.

[32] P. Poulenc and G. Giepka, in: *Nouveau Traité de Chimie Minérale*, Vol. 19, eds. R. Charonnat et al. (Libraires de l'Académie de Médecine, Paris, 1958) p. 283.

[33] R.L. Schneider, R.F. Howe and K.L. Watters, Inorg. Chem. 23 (1984) 4593.

[34] L. Huang and Y. Xu, J. Nat. Gas Chem. 6 (1997) 188.

[35] L. Huang and Y. Xu, J. Nat. Gas Chem. 6 (1997) 198.